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LOW WORK FUNCTION CsI COATINGS FOR ENHANCED FIELD EMISSION PROPERTIES (POSTPRINT)

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Low work function CsI coatings for enhanced field emission properties

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Thin films of cesium iodide (CsI) were deposited by pulsed laser deposition and by thermal evaporation onto Si substrates and were characterized by x-ray diffraction, x-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy, and Kelvin probe measurements. The thermally evaporated films were found to be stoichiometric whereas the pulsed laser deposited films showed the presence of a Cs/CsI mixture. The latter is supported by UPS measurements whose Fermi edge indicates the presence of a metallic component (elemental Cs). The presence of a Cs/CsI mixture is also supported by the Kelvin probe work function values found to be in the range of 2.6–2.8 eV, a value in excess of the 2.1 eV reported for elemental Cs. This paper addresses the physical mechanisms responsible for the presence of the elemental Cs in the films and its ramification to their field emission properties. © 2011 American Vacuum Society.

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I. INTRODUCTION

Field emission (FE) sources are used in numerous applications including display devices, x-ray tubes, charged particle accelerators, and high power microwave devices. FE sources have a number of advantages over more conventional thermionic devices including simpler construction, minimal cooling (resulting in lighter weight devices), potentially smaller beam emittance, and more consistent operation. The performance of FE sources can be enhanced by two methods. The first entails using source materials with a large aspect ratio (and correspondingly large electric field at the tip), thereby reducing the width of the potential barrier through which electrons tunnel during FE. Shiffler *et al.*¹ adopted this approach by using cathodes consisting of carbon fibers in the form of a velvet. Their carbon velvet cathodes were reported to have superior lifetimes and to exhibit lower outgassing than those fabricated from polymer velvets.

The second method of enhancing FE is to apply a coating to the cathode surface. This is thought to lower the effective surface work function (WF), thereby reducing the height of the tunneling barrier. Shiffler *et al.*^{2–4} reported using CsI films to enhance FE from carbon fibers and found that using such coatings resulted in reduced outgassing as well as improved emission uniformity. Even more interesting was the

truly remarkable reduction⁵ (by two orders of magnitude) in turn-on voltage of carbon fiber-based FE devices brought about by the application of CsI coatings.

The practical use of CsI films to enhance FE requires that the coated cathodes first be conditioned through an iterative process in which the applied voltage is increased in a step-wise manner. That is, the applied voltage is increased to a set value and held at that value for some time; the emission current is initially quite erratic but eventually attains a consistent and stable value. After the emission current stabilizes, the voltage is increased and the process is repeated. After conditioning (which can require several hours), the emission current is stable. The two order of magnitude reduction in turn-on voltage mentioned previously occurred only after the cathodes had been subjected to conditioning. This suggests that, as initially deposited, stoichiometric CsI films do not enhance field emission. This is indicated by the empirical fact that enhancement is not observed until conditioning has been carried out. This implies that the process of conditioning causes a change to the CsI surface, and it is this modified surface that is responsible for the field enhancement. Insight into the nature of the modified surface is vital to understanding the mechanism for FE enhancement through the application of CsI coatings. This is an especially pertinent question since bulk CsI is an insulator [band gap=6.2 eV (Ref. 6)] that would be expected to impede, rather than to enhance, electron tunneling.

Vlahos *et al.*⁷ investigated this question from a theoretical viewpoint by carrying out *ab initio* calculations of CsI molecules adsorbed onto graphite surfaces. Their results indicated that CsI molecules that are adsorbed vertically (oriented with the I atoms closer to the graphite surface) in a very thin layer result in a decrease in the effective WF of the surface by over 3 eV, producing an effective WF as low as

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1.22 eV. This reduction was caused by the formation of a net dipole at the graphite surface. This theoretical prediction was confirmed experimentally by Hitzke *et al.*⁸ and by Pülm *et al.*,⁹ who recorded ultraviolet photoelectron spectroscopy (UPS) spectra from CsI layers of different thicknesses on a W(100) surface. They observed an initial reduction in WF with increasing layer thickness; the WF attained a minimum value of ~ 2 eV, after which it increased with thickness. Unfortunately, in neither report the authors were able to determine the absolute CsI coverage that resulted in a minimal WF.

Vlahos *et al.*¹⁰ later carried out *ex situ* experimental characterization of the surfaces of CsI-coated cathodes after use in a FE device. Their results showed the presence of Cs and O as well as the conspicuous absence of I on the surfaces of used cathodes. These authors concluded that Cs oxides, and not CsI, were responsible for the dramatic decrease in turn-on voltage. These same authors carried out *ab initio* calculations of the adsorption of several Cs_xO_y species on graphite surfaces. Their theoretical results indicated that thin Cs oxide surface layers can result in significant reduction in the effective surface WF, thus confirming their experimental conclusions.

Additional insight was provided by Shiffler *et al.*,⁵ who examined the morphology of used CsI-coated cathodes. They reported the presence of a glassy film that appeared to have wetted the carbon cathode surface. Drummy *et al.*¹¹ carried out *ex situ* characterization of the morphology and composition of used cathodes. Their results showed the presence of Cs oxides and CsIO on the emitting surfaces. Together, *all of the previous experimental studies indicate that the surface responsible for enhanced FE performance is most likely not stoichiometric CsI.*

The purpose of the work presented here was to identify the nature of the activated surface produced by the conditioning process. The experiments entailed fabricating model structures consisting of CsI thin films on Si substrates. The CsI films were deposited by thermal evaporation (TE) and by pulsed laser deposition (PLD). The composition of the resulting films was determined (both *ex situ* and *in situ*) by x-ray photoelectron spectroscopy (XPS). The film WF was determined *in situ* by UPS and by Kelvin probe (KP) measurements. The results indicate that the formation of elemental Cs, by x-ray induced I desorption from CsI, is one potential mechanism for enhancing field emission.

II. EXPERIMENT

Substrate samples consisted of *p*-type silicon wafers ($1 \times 1 \text{ cm}^2$). Before deposition, wafers were rinsed with copious amounts of acetone and methanol and were immediately placed under vacuum. CsI films were deposited in two different PLD chambers. The first chamber consisted of a stand-alone deposition system. The second chamber was attached to surface analysis system that allowed *in situ* analysis. Both deposition chambers reached a background pressure of at least 6.65×10^{-6} Pa before deposition. Both PLD systems were also equipped with a rotating target with the substrate

placed approximately 5–10 cm away from the target. The PLD targets were positioned at approximately 45° from the substrate surface normal. The stand-alone system was also equipped with a thermal evaporator. The thermal evaporator consisted of quartz crucible that was resistively heated by a tungsten wire. The deposition rate was determined with thin film deposition monitor. Film thicknesses were in the 15–30 nm range; the results presented here were independent of thickness. During evaporation the operating pressure was 1.33×10^{-4} Pa.

A Lambda Physik LPX 305 excimer laser with a wavelength of 248 nm and pulse width of 25 ns was used for laser deposition in both chambers. The laser was pulsed at 1 Hz. A deposition rate of 0.5 nm/pulse was determined with the thin film deposition monitor. During ablation, the operating pressure ranged $1\text{--}4 \times 10^{-5}$ Pa. All depositions were carried out in vacuum with the substrates at room temperature.

Ex situ analysis was done in an SSI M-probe XPS system. Background pressure in the analysis chamber was better than 2.66×10^{-7} Pa. Data were collected with an Al $K\alpha$ (1486.6 eV) monochromatized source. The binding energy scale was calibrated against Cu $2p_{3/2}$ and $3s$ binding energies at 932.6 and 122.0 eV, respectively. Resolution was determined using the full width at half maximum (FWHM) of the Au $4f_{7/2}$ line which came out to be 0.71 eV. The pass energies of survey and high resolution scans were collected at 100 and 50 eV, respectively.

In situ analysis data were collected with a Staib surface analysis instrument equipped with a DESA 150 analyzer. Background pressure in the analysis chamber was better than 4.0×10^{-8} Pa. The analysis chamber was separated from the deposition chamber by a gate valve. Immediately after deposition, samples were transferred into the analysis chamber without exposure to air. The instrument was capable of collecting XPS, Auger electron spectroscopy, and UPS data. For XPS data were collected with a standard Mg $K\alpha$ (1254.6 eV) source. The energy scale was calibrated against Au $4f_{7/2}$ and Cu $2p_{3/2}$ at binding energies of 84.0 and 932.6 eV, respectively. XPS resolution was determined by the FWHM of the Au $4f_{7/2}$ line which came out to 1.2 eV. The pass energies for survey and high resolution scans were 80 and 20 eV, respectively. Auger scans were recorded in undifferentiated mode at a resolution of 0.2%. For UPS, the He I (21.2 eV) line was generated with a differentially pumped Specs 10/35 He discharge lamp. The Fermi edge was calibrated against a sputter cleaned gold sample. Resolution, obtained from the width of the Fermi edge, was determined to be 300 meV. UPS data were collected with a negative bias applied to the substrate in order to obtain the true WF of the deposited film.

All data were processed in CASAXPS. The XPS data were background corrected with the Shirley background,¹² and components were fitted to each spectrum using a Levenberg–Marquardt algorithm that minimizes χ^2 . Each component consists of a convolution of the Gaussian and Lorentzian functions. Auger data were differentiated with a Savitzky–Golay¹³ routine using five data points.

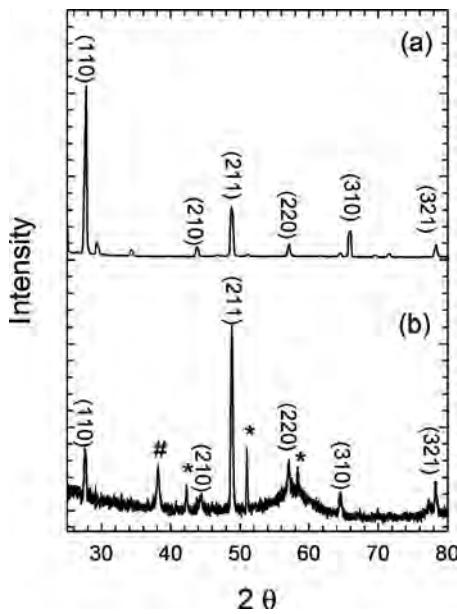


FIG. 1. XRD results of CsI films deposited by (a) thermal evaporation and (b) pulsed laser deposition. The indicated reflections are assigned to CsI. The peaks denoted by asterisks are assigned to Cs₂O and those denoted by the # symbol are assigned to CsIO₃. The broad peak centered near 58° is an artifact of the sample mounting procedure in the diffractometer.

The x-ray diffraction (XRD) measurements were performed in the Bragg Brentano parafocusing geometry on a PANalytical X'Pert Pro MRD system using the 4 in. wafer stage. The incident beam optics consisted of a Cu $K\alpha$ source operated at 45 kV and 40 mA. The diffracted beam optics consisted of a 0.18° parallel plate collimator with a 0.04 rad Soller slit and a scintillation detector. 2θ scans were acquired for all samples with an incident angle of 7°.

The WF of the thin films was measured *in situ* using a McCallister KP-6500 Kelvin probe¹⁴ with a stainless steel tip with a 5 mm diameter. The procedure involved first determining the WF of the tip using UPS. The WF tip value was found to be 4.8 eV. The absolute value of the film WF was then determined by the difference between the KP tip and the sample as recorded in the KP experiments.

III. RESULTS AND DISCUSSION

A. XRD, XPS, and UPS results

Shown in Fig. 1 are the XRD results. Presented in Fig. 1(a) is an XRD scan acquired from a CsI film deposited by TE. The scan exhibits a number of intense, sharp peaks which are assigned to the indicated Bragg reflections from CsI.¹⁵ The presence of these peaks indicates the deposition of polycrystalline, stoichiometric CsI by TE. This is reasonable given that TE is the method of choice for alkali halide deposition.¹⁶ In addition, Butman *et al.*¹⁷ investigated by mass spectrometry the vapor composition during free-surface vaporization of CsI and reported it to consist primarily of CsI molecules (~90%) with a smaller percentage (~10%) consisting of CsI dimers. That TE of CsI forms a stoichiometric film is therefore not unexpected.

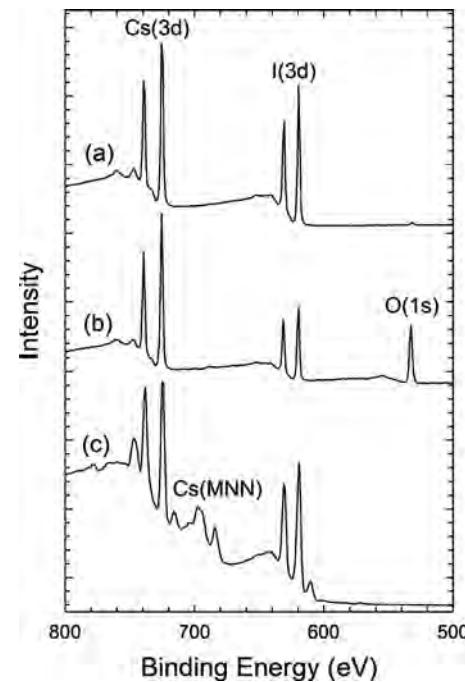


FIG. 2. XPS survey scans of CsI films deposited by (a) thermal evaporation and acquired *ex situ*, (b) pulsed laser deposition and acquired *ex situ*, and (c) pulsed laser deposition and acquired *in situ*.

Presented in Fig. 1(b) is an XRD scan from a CsI film deposited by PLD. The broad peak centered near 58° is an artifact caused by the sample mounting procedure. The scan contains several sharp, intense peaks that are assigned to the indicated Bragg reflections from CsI.¹⁵ These peaks indicate the presence of polycrystalline, stoichiometric CsI in the film deposited by PLD. In addition, the scan contains other peaks (denoted by asterisks) that are assigned to Cs₂O (Ref. 18) and to CsIO₃ (Ref. 19) (denoted by the # symbol). These results indicate that PLD of CsI produces a film containing a mixture of CsI, Cs₂O, and CsIO₃. Given the energetic nature of PLD, it is expected that the flux of ablated material would contain a wide variety of species including not only molecular CsI but also numerous atoms, radicals, and ions with hyperthermal kinetic energies. That Cs₂O is detected in the deposited film suggests the presence of elemental Cs in the nascent deposited film that was subsequently oxidized upon air exposure to form Cs₂O.

Presented in Fig. 2 are XPS survey scans of the deposited films. The spectrum shown in Fig. 2(a) was acquired from a CsI film deposited by TE and was acquired *ex situ*. The spectrum contains Cs (3d) and I (3d) peaks plus a small O (1s) peak. The small amount of O is most likely due to reaction with atmospheric H₂O during sample transfer from deposition to the analysis chamber. The relative elemental ratios are given in Table I; the I/Cs ratio calculated from the relative peak intensities was 0.82, indicating the deposition of near-stoichiometric CsI by TE. This result is consistent with those from XRD; TE results in deposition of stoichiometric CsI. That the film deposited by TE is apparently somewhat I deficient is attributed to air exposure of the deposited film prior

TABLE I. Summary of XPS results.

Sample	I/Cs ratio	O/Cs ratio
TE	0.82	0.22
PLD (<i>ex situ</i>)	0.51	5.1
PLD (<i>in situ</i>)	1.0	...
PLD target	0.97	0.07

to XPS analysis. This is consistent with the XPS results from the PLD target, which are also presented in Table I, where it can be seen that the I/Cs ratio from the stoichiometric, air-exposed target is also somewhat less than unity. This is discussed later.

Presented in Fig. 2(b) is an XPS survey scan acquired from a CsI film deposited by PLD. The spectrum, which was acquired *ex situ*, contains Cs (3d), I (3d), and O (1s) peaks; the relative elemental concentrations calculated from the peak intensities are presented in Table I. The I/Cs ratio of this film is 0.51 and is considerably smaller than that from the film deposited by TE. Even more interesting is the significantly higher relative O concentration for this film. This result is consistent with those acquired from XRD analysis and suggests that the nascent film deposited by PLD contained some elemental Cs and the elemental Cs component was subsequently oxidized upon air exposure.

Shown in Fig. 2(c) is an XPS survey scan acquired from a CsI film deposited by PLD. This spectrum was acquired *in situ*, a few minutes after deposition. In addition to the Cs (3d) and I (3d) photoelectron peaks, this spectrum contains Cs (MNN) Auger peaks, which were not present in Figs. 2(a) and 2(b) since a different x-ray source anode was used for the two sets of spectra. The relative elemental concentrations calculated from these data are presented in Table I. The I/Cs ratio is unity, and the relative O concentration is below the XPS detection limit. These results confirm that Cs and I were indeed stoichiometrically transferred from target to substrate during deposition. The question of the chemical state(s) of the deposited Cs remains.

Presented in Fig. 3(a) is a high resolution scan of the Cs (3d_{5/2}) peak from the CsI film deposited by PLD and acquired *in situ*. The peak is broadened and is composed of two components. The lower binding energy component (appearing near 724 eV) arises from Cs bound to I.²⁰ The higher binding energy component (appearing near 726 eV) arises from elemental Cs.²¹ These results confirm the hypothesis that PLD-deposited films contain elemental Cs in addition to CsI. Additional indirect evidence for this is presented in Fig. 3(b), which is a high resolution Cs (3d_{5/2}) scan recorded after the same PLD film had been removed from the analysis chamber, exposed to air for 5 min, and reanalyzed. The disappearance of the elemental Cs peak after air exposure confirms the presence of elemental Cs in the as-deposited film. The Cs (3d_{5/2}) binding energies in CsI and Cs₂O are very similar and are not distinguishable by XPS.

Presented in Fig. 4 are *in situ* UPS results acquired from a PLD-deposited film. The spectrum exhibits Cs (5p) and I

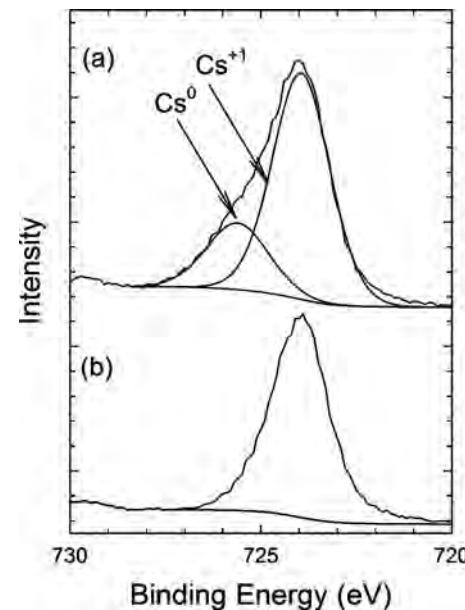


FIG. 3. High resolution XPS results from CsI film deposited by PLD. The spectra were acquired *in situ* and show the Cs (3d_{5/2}) peak (a) immediately after deposition and (b) after 5 min exposure to air. The spectrum presented in (a) shows the presence of metallic Cs.

(5p) peaks as well as a secondary electron cutoff at higher binding energy. The features in this spectrum are in good agreement with those reported on bulk CsI by Poole *et al.*⁶ as well as with UPS results of CsI thin films of various thicknesses reported by Hitzke *et al.*⁸ and by Pülm *et al.*⁹

The XRD and XPS results indicate that TE of CsI forms a stoichiometric film of the material. In contrast, the nascent films formed by PLD contain a mixture of CsI and elemental Cs. The presence of equal (total) amounts of Cs and I in the nascent deposit and the presence of elemental (i.e., unreacted) Cs in the deposit implies that the PLD film also con-

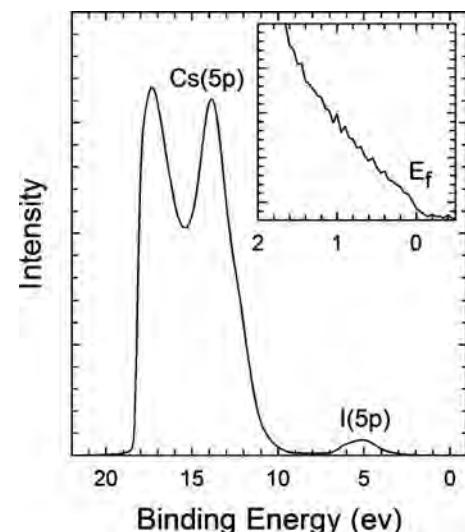


FIG. 4. UPS results of CsI film deposited by PLD. The spectrum was acquired *in situ*. The inset shows the region in the vicinity of the Fermi edge. The WF of the sample derived from this spectrum was 2.7 eV.

tains unreacted iodine, presumably existing as I_2 . We hypothesize that I_2 , upon air exposure, reacts with atmospheric H_2O to form HI , which then leaves the surface as a gas. Elemental Cs, also present in the nascent film, will react with atmospheric H_2O or O_2 to form Cs_2O which would remain on the surface. The net result would be the formation, after air exposure, of a film that contains a mixture of CsI and Cs_2O and whose surface is I deficient. This description is in excellent agreement with the XRD and XPS results presented in Figs. 1(b) and 2(b), respectively. We hypothesize that a similar surface reaction occurred on the surface of the film deposited by TE.

B. Work function measurements

From the UPS spectrum shown in Fig. 4, we extracted a WF of 2.7 eV for the as-deposited PLD CsI thin films. This value is in excellent agreement with the KP measurements which were repeatedly found to be between 2.6 and 2.8 eV for thin films grown under similar PLD conditions.

We believe that the low WF of these films is due to the free Cs within the films. This conjecture is supported by (1) the fact that the films appeared bluish right after extraction from the chamber, a characteristic of Cs samples, and (2) the existence of a well defined Fermi edge in Fig. 4, indicative of a metallic component (free Cs) in the film. Furthermore, the fact that the WF of the CsI surface measured *in situ* is larger than the reported 2.1 eV for pure Cs is consistent with the presence of a Cs/CsI mixture in the films, in agreement with the UPS and XPS results. Due to the presence of CsI with a high WF and the fact the KP probe measures an average of the WF over the area of the probe, the resulting WF of the thin film is indeed expected to be larger than 2.1 eV.

It was observed that the WF of the PLD grown CsI thin films degrade rapidly when the KP measurements were recorded continuously after bleeding some air in the chamber. In that case, the WF of the CsI film continuously increased above 4.0 eV. We observed that the CsI films exposed to air after extraction from the chamber progressively turn milky which seems to indicate the presence of CsO and Cs_2O in the thin films, as supported by our XPS analysis discussed above.

Additionally, *in situ* KP measurements were recorded on a TE grown CsI thin film. The *in situ* KP recorded a WF value of 4.7 eV, roughly 2 eV higher than the films grown by PLD. This is consistent with the assumption that TE grown CsI is stoichiometric and would thus be expected to have a higher WF than PLD grown films which are Cs rich. Exposure to atmosphere resulted in a slight decrease in WF to 4.6 eV, as compared to the PLD grown film which showed a significant increase in WF on exposure to atmosphere.

C. Radiation-induced film modification

The results presented heretofore indicate that stoichiometric films of polycrystalline CsI, deposited by TE, have a WF of 4.7 eV and do not exhibit FE under the conditions employed here. Thin films of CsI, deposited by PLD, have a significantly lower WF, contain some elemental Cs, and do

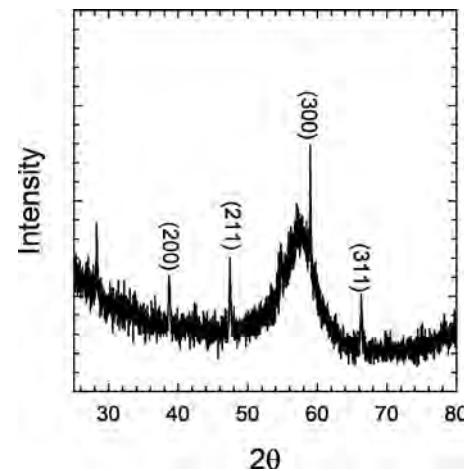


FIG. 5. XRD results of CsI film deposited by PLD. The spectrum was acquired from 16 h of continuous x-ray exposure. The peaks are assigned to reflections from $CsIO_3$. The broad peak centered near 58° is an artifact of the sample mounting procedure in the diffractometer.

exhibit FE. These data suggest that elemental Cs may be an important component of the active, electron-emitting surface formed during conditioning. The presence of elemental Cs is also consistent with the observation by Shiffler *et al.*⁵ of a glassy, wetting layer on the surface of used cathodes; Cs would likely be present as a liquid on the surface of an operating cathode given its low melting point (28 °C). The question remains of how, in real FE devices, would elemental Cs be formed from a CsI film?

One indication is presented in Fig. 5, which is an XRD scan from a PLD-deposited film. In this case, the sample was kept in the XRD spectrometer and was irradiated for 16 h with $Cu K\alpha$ (8.1 keV) radiation. The broad feature centered near 58° is an artifact of the sample mounting procedure. The signal-to-noise ratio of this spectrum is less than those presented previously, indicating less crystallinity in this sample after x-ray bombardment than those presented earlier. There are several peaks in the spectrum which can be assigned to reflections from $CsIO_3$.¹⁹ There is no indication of CsI in this heavily irradiated film. Shown in Fig. 6 is an XPS survey scan (*acquired ex situ*) of the same heavily irradiated sample. The striking feature of this spectrum is the complete absence of I on the surface of the film that was exposed to x-ray bombardment. Both spectra show that significant changes can occur in CsI film chemistry upon exposure to x-ray irradiation.

A field emission system consists of a cathode and an anode with a potential difference between the two. Operation of such a device results in bombardment of the anode by high energy electrons. This results in the emission of both characteristic x rays from the anode and in the emission of bremsstrahlung as the high energy electrons decelerate upon collision with the anode. We hypothesize that these high energy x rays (characteristic and bremsstrahlung) are one energy source responsible for the depletion of I from the CsI surface.

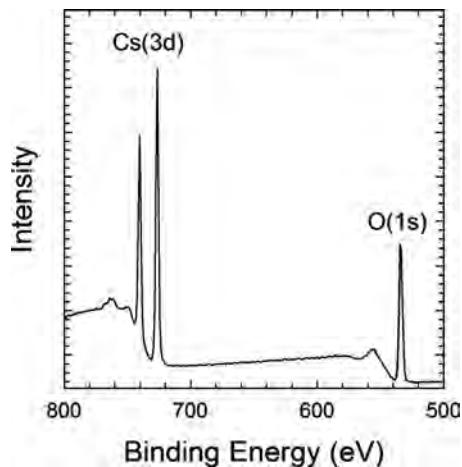


FIG. 6. XPS survey scan of CsI film deposited by PLD. The sample was exposed to 16 h of continuous x-ray exposure prior to this spectrum.

It has been known for some time that alkali halides are susceptible to radiation damage through a process denoted desorption induced by electronic transitions.²² Desorption can be induced by high energy electrons, ions, and photons. The exact mechanism depends on the nature of the impinging particle as well as the target material. In the present case of CsI, we hypothesize that preferential I desorption is initiated by the formation of an I core vacancy as a result of x-ray photoabsorption. The core vacancy relaxes by an Auger process in which a higher-lying I electron drops into the vacancy, and a second higher-lying electron is ejected from the I atom. The net result is the conversion of I⁻ into I⁺. I⁻ is bound within the CsI matrix by an attractive Madelung potential. Nascent I⁺, on the other hand, would experience a repulsive potential and would be ejected from the surface by this potential. In an operating FE device, I⁺ would be initially ejected from the surface by the Coulomb repulsion with the neighboring Cs⁺ species but would return to the cathode surface because of the applied electric field; it is likely that the I⁺ would return to a region of the surface different than its origin. The net result would be the formation of a Cs-rich region whose work function would be less than that of CsI, which would enhance FE. This scenario predicts that x-ray bombardment of CsI will result in the ejection of hyperthermal I⁺. It also predicts I⁺ desorption thresholds that coincide with the I energy levels in CsI. Absorption of an x-ray photon by core levels in Cs would produce more highly ionized Cs, which would not be expected to significantly alter the surface chemistry. The depletion of I by x-ray induced bombardment is one mechanism that needs to be taken into account as part of a larger effort to understand the operation of FE devices. Other mechanisms, such as H₂⁺ ion-induced bombardment, are also likely within the electric field of an operating FE device and need to be explored.

IV. SUMMARY AND CONCLUSIONS

Thin films of CsI were deposited by PLD and TE on Si substrates and were characterized by XRD, XPS, UPS, and

KP measurements. The TE films were found to be stoichiometric, while the PLD films showed the presence of a Cs/CsI mixture. The latter is supported by the UPS measurements whose Fermi edge indicated the presence of a metallic component (elemental Cs). The presence of a Cs/CsI mixture is also supported by the recorded WF values in KP measurements which were in the range of 2.6–2.8 eV, a value in excess to the 2.1 eV reported for elemental Cs. We hypothesize that free Cs is formed from CsI in FE devices following x-ray bombardment; the x rays originate at the anode as a result of bremsstrahlung and as characteristic x rays from the anode material. It is conjectured that this Cs formation occurs during cathode conditioning.

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